**Dissolution of Nitrides and Precipitation of an Austenitic Phase on the Surface of Fe-20%Cr alloys**

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**Abstract**

New phases have been observed on surfaces of metal specimens during cooling after heat treatment at 1200, 1300 and 1400 °C of an Fe-20mass% Cr alloy with different nitrogen contents (65, 248 and 490 ppm) and deoxidised by Ti and Zr. These phases were assumed to be related to a phase transformation. The analysis of nitrogen content in matrix metal and new phase crystals was carried out based on point analysis of nitrogen using SEM. According to obtained results it was concluded that the nitrogen had been dissolved from the nitrides during 60 minutes of heat treatment at high temperature and diffused in to the matrix. These areas of enriched nitrogen content were then transformed to a new phase during cooling. This new phase was assumed to be austenite because the nitrogen is a well known element for promotion of austenite formation. The possibility of austenite formation in Fe-20mass% Cr alloys with different nitrogen content was considered and confirmed thermodynamically by using the Thermo-Calc software.

**Keywords**: ferritic stainless steel, high Cr alloy; Ti and Zr deoxidation; N content, austenite.
1. **Introduction**

High chromium stainless steels with low alloying contents of the austenite forming alloying elements (such as Zn, Cu, Ni, Mn, N and C) likely occur as ferritic stainless steels from solidification temperature down to room temperature.\(^1\) There are, although, some aspects to consider when discussing special elements which can occur as precipitations, i.e. Nitrogen and Carbon. The effect of Nitrogen and Carbon contents on the precipitation is dependent on the distribution in the steel matrix. If precipitated as nitrides or carbides, the structure is more or less independent of the content. At the same time, if N or C are dissolved, it can change the structure from pure ferritic to pure austenitic\(^2\-^3\). These phenomena have become interesting when the steel is under the influence of an increased temperature. Different precipitations can act differently and be more or less stable.

These phenomena can be of great importance when a ferritic stainless steel is under the influence of high temperature changes. New precipitations can have a significant effect on the corrosion properties of the steel after i.e. welding.

Boundary migration and pinning effect of particles during heat treatment of Fe-20mass% Cr alloys at 1200, 1300 and 1400 °C were investigated in a previous
study\textsuperscript{[4]}. Dissolution of nitrides in metal specimens with different nitrogen contents during heat treatment experiments was also investigated\textsuperscript{[4]}.

The purpose with the present study was therefore to investigate the precipitation mechanism and to identify the new phase. The number and composition of the inclusions in the metal were changed by varying the nitrogen content in the samples. The dissolution of nitrides where observed as a reduced pinning effect\textsuperscript{[4]} together with heterogeneities in the structure and precipitation of small areas with austenite. The dissolution behavior of the nitrides and pinning effect of particles were determined based on the in-situ observations by using a CSLM.

2. **Experimental work**

2.1. **Sample Preparation**

Three groups of Fe-20 mass\% Cr samples with different nitrogen contents were made by melting electrolytic Fe and pure Cr metal in an arc furnace under an Ar atmosphere. A part of each group samples (150 g) was re-melted in an induction furnace at 1600°C and deoxidised by Ti and Zr. After addition of deoxidants, and stirring for homogenisation of chemical composition, the melt was
cooled to 1400°C at a cooling rate of 0.8°C/s, followed by quenching in water. The final total nitrogen contents in the obtained ingot samples were 65, 248 and 490 ppm, respectively, with an oxygen content of approximately 150 ppm in all samples. Detailed description of melting procedure is given in previous paper.\textsuperscript{[5]}

After etching and verification of equiaxed grain zone, four pieces were cut from the equiaxed zone of horizontal slices in each ingot sample. One metal piece was used for determination of particle content and composition by observation on surface of film filters after electrolytic extraction.\textsuperscript{[5]} The other three pieces from each ingot (totally 9 pieces from three ingots, hereafter named specimens 1a, 1b, 1c, 2a, ..., 3c) were cut in the shape of cylinders (Ø4.2 x 1.5 mm) for heat treatment experiments in a Confocal Scanning Laser Microscope (CSLM). Specimens 1a, 1b and 1c were heated in CSLM chamber under pure Ar atmosphere to 1200, 1300 and 1400°C, respectively. Basic experimental conditions for heat treatments of different metal samples are given in Table 1. The procedure was repeated with specimens of ingot samples 2 and 3. Each specimen was kept at the experimental temperature for 60 minutes followed by cooling down to room temperature. The changes of temperature and cooling rate during cooling of specimens from different experimental temperatures down to 500°C are shown in Figures 1 and 2.
During cooling of the specimens, a precipitation of new phase was observed directly on metal surface. More experimental details of the in-situ observation during heat treatment in the CSLM are given elsewhere.[4]

2.2. Examination of New Phases

The specimens after heat treatment experiments were observed and the micrographs of the new phases were taken by using a Scanning Electron Microscope (SEM) equipped with an Electron Probe Micro Analyzer (EPMA). A computer based image analyzing software (Winroof©) was used to analyze the area fraction (in %) of the new phase on a surface of metal specimens. A SEM equipped with Wave length Dispersive Spectrometry (WDS) was used for characterization of the new precipitated phase. Determination of the chemical composition of the new phase was performed with focus on the composition differences between N contents in the matrix and the new phase.
2.3. Thermodynamic Calculations of New Phase Formation

Passing the gamma loop during cooling or heating in the binary Fe-Cr phase diagram in Fig. 3 results in an austenitic transformation. The loop is proven to be enlarged by dissolved nitrogen\cite{2-3} resulting in Cr-contents much higher than the 13-14\% representative for the maximum Cr-content in the binary phase diagram. In order to explore the extension of the gamma loop and the possibility of forming new phases during cooling of Fe-20mass\% alloys with different nitrogen contents, the Thermo-Calc software was used. Based on the information from the WDS analysis of the new phases, a series of vertical sections were calculated in the Fe-Cr-N system using 50, 300, 500, 6000 and 10 000 ppm N. For each vertical section, the total nitrogen content was fixed (to one of the above values), the total number of mole of atoms in the system was fixed to 1 and the pressure was set to $10^5$ Pa (1 bar). The total mass fraction of Cr and absolute temperature were used as starting conditions and as axes in the automatic mapping procedure performed by the software. The thermodynamic descriptions of the phases were taken from the TCFE4 database, the most recent updated database for Fe-alloys, distributed together with the Thermo-Calc software. In order to get accurate calculations, small step sizes had to be used. The mass fraction was varied with $10^{-3}$ and the
absolute temperature with 1K. Finally, the calculated results were plotted as weight percent Cr and temperature Celsius.

3. Results and Discussion

The grain boundary, which is revealed by thermal etching (thermal groove)\(^7-8\) at high temperature, starts to be visible in a CSLM after approximately 800 °C. In addition, it becomes clearer with an increased temperature (more than 1100°C).

The pinning effect of particles clearly decreased with an increased heat treatment temperature, as is described in a previous paper.\(^4\) It was shown that the growth of grain on a surface of metal specimens almost stops after 60 minutes of holding time at high temperature (1200, 1300 and 1400°C). It is believed that the metal system (the grain growth and pinning effect of particles) in practice approaches an equilibrium condition. However, during cooling of the heat treated specimens, some small regions of a new phase appeared and could be observed by microscope system of CSLM. The consideration of the formation of a new phase in Fe-20mass% Cr alloy and in ferritic stainless steels after heat treatment is given below.
A comparable analysis of temperature profile and cooling rate of different specimens after heat treatment are shown in Figures 1 and 2 for metal specimens with 248 ppm of nitrogen (Exps. 2a, 2b and 2c). As shown in Fig. 2a, the data points of calculated cooling rate for Exp.2c specimen has a significant dispersion, particularly in period from 5 to 25 s of cooling time. However, the temperature profile during cooling of this specimen (Fig. 1) is very smoothed. The same tendency is observed for all other specimens. This significant scatter of data points for different cooling rates can be explained by some inert temperature measurement and renewal of updated fixed data on the screen of CSLM. It can be seen in Fig. 2b that the total cooling rates of all metal specimens after holding at 1200, 1300 and 1400°C are very similar. They do not show some deviation (such as peak or shelf) from a smoothed curve. This means that all specimens were cooled for almost the same conditions.

During cooling of heat treatment experiments at 1300°C, the precipitation of a new phase on the surface of metal specimens was observed directly at 825 and 864°C for Exp.2b ([T.N] = 248 ppm) and Exp.3b ([T.N] = 490 ppm), respectively. For heat treatment experiments at 1400°C, the precipitation of a new phase was fixed visually at 1127°C for Exp.2c ([T.N] = 248 ppm) and 1143°C for Exp.3b. 
(\[T,N\] = 490 ppm). By direct observation of other experimental specimens during cooling (particularly of metal specimens with 65 ppm of N), it was difficult to fix visually the moment of formation of a new phase due to the very small size of precipitated phase in these experiments. Because of the absence of oxygen or nitrogen in the experimental atmosphere (pure Ar atmosphere) in CSLM chamber, the precipitation was concluded to be originated from the composition of the steel and the heat treatment parameters.

The temperatures, which are fixed during direct observations of new phase formations in Exps. 2b, 2c, 3b and 3c, were recalculated according to the obtained results for temperature calibration experiments in CSLM. The corrected temperature for nucleation of a new phase on a metal surface of Fe-20mass% Cr specimens are given in Table 1. The data ranges from about 860 to 900°C for heat treatment experiments at 1300°C and from 1130 to 1150°C for experiments at 1400°C.

The characteristics of the new phase (such as area fraction, morphology, size and N content) were investigated more precisely on the metal surface of specimens after finishing of heat treatment experiments by using SEM at higher magnifications. The area fraction (in %) of the new phase on the metal surface was
determined by using image analyzing software (Winroof©). According to obtained results, the area fraction of new phase crystals on surface of metal specimens is varied in the range from 1 to 5 % for heat treatment experiments at 1200°⁰C, from 7 to 16 % for experiments at 1300°⁰C and from 4 to 11 % for experiments at 1400°⁰C. It was found that the value of the area fraction depends first of all on the morphology of precipitated new phase crystals.

It should be pointed out that new phase crystals have a different morphology for different heat treatment experiments at various temperatures. The typical micrographs of new phase with different shapes are shown in Table 2 for various N contents in metal specimens and heat treatment temperatures. It can be seen that the shape of the precipitated new phase (hereinafter called “Type 1”, “Type 2” and “Type 3” which have “leaf”, “flower” and “dendrite”-shapes, respectively) changes according to the temperature of heat treatment experiments. Furthermore, it is practically independent on the N content in metal specimens. It should be pointed out that all types of new phases can be found on the surface of metal specimens for heat treatment experiments at different temperatures. However, most of the new phase crystals for 1200°⁰C experiments have Type 1, for 1300°⁰C – Type 2 and for 1400°⁰C – Type 3.
One of the possible explanations of relationship between the morphology of precipitated new phase and the temperature of heat treatment experiments is discussed below. All specimens have almost the same cooling rate curves (Fig. 2b). However, the values of cooling rate, which correspond to the temperature intervals for appearance of new phase, are different. More specifically, they equals to 18-20 and 40-43 °C/s for experiments at 1300 and 1400°C, respectively. Based on these results, it may be concluded that the morphology of the precipitated new phase depends above all on the cooling rate of metal specimens and the heat treatment temperature.

However, the size of new phase crystals depends significantly on the nitrogen content in the metal specimens. The size of the new phase crystal, $D_{\text{NP}}$, was determined as the equivalent diameter of a circle having the same area as the image of the measured crystal on the SEM micrograph. It was found that the average value of $D_{\text{NP}}$ increases with an increased N content. For example, the average size of new phase crystals increases. More specifically, the $D_{\text{NP}}$ values were 1.86, 4.24, and 4.92 µm for metal specimens having the 65, 248 and 490 ppm of N, respectively. A similar tendency was obtained also for precipitated new phase for heat treatment experiments at temperatures of 1200 and 1400°C.
For clarification and understanding of this relationship, the content of nitrogen in the metal matrix and the new phase crystals was determined by point analysis using a SEM equipped with WDS. The typical micrographs and content of nitrogen in different analysed zones of the matrix metal and the new phase crystals are shown in Figures 4, 5 and 6 for Types 1, 2 and 3, respectively. Overall, it can be seen that the N content in all new phase crystals is significantly larger than that in the metal matrix. The relation between the N content, which was obtained by analysis of different zones of metal matrix and different type crystals, and the distance from the boundary of new phase are shown in Figure 7. It was found that the content of nitrogen in the metal increases slowly when approaching the boundary of the new phase. Furthermore, it jumps to a value of 0.2 % on this boundary. Then, as the center of new phase crystal is approached, the [% T.N] value continues to significantly increase until up to a value of 0.22-0.25% for Type 1 crystals, 0.5-0.7% for Type 2 crystals and 1.0-1.8 for Type 3 crystals. However, these N contents in the new phases are much smaller in comparison with those present in pure TiN (22.6% N) and ZrN (13.3% N) particles.

According to the obtained results, it may be concluded that the nitrogen had been dissolved from the nitrides during 60 minutes of heat treatment at high
temperatures and diffused in to the matrix. These local zones of enriched nitrogen content were then transformed to a new phase during cooling. The morphology of the precipitated new phase crystals depends on the N content in the local enriched zone and cooling rate of the metal specimen. This relationship is shown schematically in Figure 8.

Based on the obtained results, it can be assumed that this new phase is an austenite phase because nitrogen is a well known element for promotion of austenite formation in ferritic stainless steel.[1-2] In order to support this statement, the thermodynamic possibility of austenite formation in Fe-20mass% Cr alloy with different nitrogen content is considered below.

3.2. Thermodynamic Consideration of New Phase Formation

The changes in the binary Fe-Cr diagram could be observed by gradually increasing nitrogen content in calculations. This is illustrated in Figure 9, for calculations based on the total nitrogen content observed in the specimens. As can be seen, the gamma loop (representing ferrite to austenite transformation i.e. bcc \( \rightarrow \) fcc) is growing towards higher Cr-contents when the nitrogen content is
increased. These calculations show that more than 300 ppm of nitrogen is enough for austenite formation at around 1000 °C for this Fe-20mass% Cr alloy. When the nitrogen content is further increased, the gamma loop extends towards both higher Cr-content as well as higher temperatures. Furthermore, the gamma loop becomes more complex and more phases can be observed in the calculations.

The calculations in Figure 10 were based on the actual composition variations analysed by WDS. More specifically, in the 6000 ppm (0.6wt %) nitrogen case, there are three to four different possible phase regions for precipitation during cooling from 1400 °C. The different shapes, compositions and morphologies, which will be discussed below, can be explained by combining these calculated phase diagrams and the heat treatment temperature data. More specifically, the 1400 °C specimen is kept at the phase region well above austenite (fcc), while the 1300 °C is close to the phase line. However, the 1200 °C specimen is instead inside the austenite phase region.

It can be assumed that diffusion of nitrogen back towards initial nitrides can occur during cooling. Thus, this may thereby determine the structure of the precipitations. Different types of precipitations have been discussed (Types 1, 2...
and 3), as seen in Table 2. Depending on the cooling rate, from ferrite through the austenite region below \( \sim 1250 \, ^\circ C \), the time for diffusion of nitrogen can be related to the different shapes and composition gradients for the different phase types. The heat treatment at 1200 \( ^\circ C \) seems to be inside the phase region of austenite in Fig. 10. Therefore, it can be assumed that phase transformations occurred during heat treatment which lead to more evenly distributed small Type 1 precipitations. For higher temperatures (above \( \sim 1250 \, ^\circ C \)), it can instead be assumed that the diffusivity of nitrogen is increased. Thus, this will lead to formations of larger precipitations during cooling. According to the upper phase diagram in Fig. 10 representing the nitrogen content analysed for the Type 2 precipitations (see Fig 8), there should be austenite and ferrite (fcc + bcc) down to \( \sim 1150 \, ^\circ C \) followed by fcc. Thereafter, fcc + Cr\(_2\)N between 1000 and 900 \( ^\circ C \). According to the lower phase diagram in Fig. 9 representing the type 3 precipitations (see Fig 8) there should be austenite and gas (fcc + G) down to \( \sim 1100 \, ^\circ C \) and thereafter fcc + Cr\(_2\)N between 1100 and 900 \( ^\circ C \). More specifically, according to Table 1, the Types 2 and 3 precipitations can be assumed to represent two different precipitated phase transformations involving austenite.
4. Conclusions

New phases have been observed, measured and investigated on the surface of metal specimens during cooling after heat treatment at 1200, 1300 and 1400 °C of an Fe-20mass% Cr alloy with different nitrogen contents (65, 248 and 490 ppm) and deoxidised by Ti and Zr. The possibility of austenite formation in the Fe-20mass% Cr alloy at different nitrogen content was considered and confirmed thermodynamically by using Thermo-Calc software. The most important specific conclusions may be summarized as follows:

1) The new phase crystals are precipitated on the surface of metal specimens of an Fe-20mass% Cr alloy with different nitrogen contents of (65, 248 and 490 ppm) during cooling, after being heat treated at high temperatures (1200, 1300 and 1400°C).

2) Three different types of new phases were observed. The content of nitrogen in new phase crystals varied in the ranges of 0.22-0.25% N for Type 1 crystals, to 0.5-0.7% for Type 2 and to 1.0-1.8 for Type 3. The morphology of the precipitated new phases depends on the nitrogen content in local zones of the metal matrix and the cooling rate of the metal specimens.
3) Thermodynamic calculations showed that the Gamma loop (representing austenite formation) was increased towards higher Cr-contents, when the nitrogen content was increased. Furthermore, it was found that austenite transformation in an Fe-20mass%Cr alloy is possible at dissolved nitrogen contents above 300 ppm.

4) According to the nitrogen contents in the new phase crystals and the results obtained by thermodynamic calculations for the Fe-20mass% Cr alloy, this new phase was assumed to be austenite.
REFERENCES


Table 1. Experimental conditions for heat treatment of different metal specimens of Fe-20% Cr alloy and temperature of new phase.

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>[T.N] (mass ppm)</th>
<th>[T.Ti]</th>
<th>[T.Zr]</th>
<th>Temperature of heat treatment* (°C)</th>
<th>Temperature of new phase observation (°C)</th>
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<tbody>
<tr>
<td>1a</td>
<td>65</td>
<td>652</td>
<td>89</td>
<td>1200</td>
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</tr>
<tr>
<td>1b</td>
<td></td>
<td></td>
<td></td>
<td>1300</td>
<td>-</td>
</tr>
<tr>
<td>1c</td>
<td></td>
<td></td>
<td></td>
<td>1400</td>
<td>-</td>
</tr>
<tr>
<td>2a</td>
<td>248</td>
<td>578</td>
<td>214</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td></td>
<td></td>
<td></td>
<td>1300</td>
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<tr>
<td>2c</td>
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<td></td>
<td>1400</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>1400</td>
<td>1143</td>
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*: holding time at high temperature during heat treatment – 60 min.
Table 2.  Typical shapes of new phase observed on surface of Fe-20% Cr alloy specimens with different total nitrogen contents.

<table>
<thead>
<tr>
<th>[T.N] (ppm)</th>
<th>Heat treatment temperature (°C)</th>
<th>Type of new phase crystal</th>
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</thead>
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<tr>
<td></td>
<td>1200</td>
<td>Type 1</td>
</tr>
<tr>
<td>65</td>
<td>1300</td>
<td>Type 2</td>
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<tr>
<td>248</td>
<td>1400</td>
<td>Type 3</td>
</tr>
<tr>
<td>490</td>
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</table>
Figure 1. Temperature profile of metal specimens with 248 ppm of N during cooling after heat treatment at different temperatures.
Figure 2. Cooling rate of metal specimens with 248 ppm of N after heat treatment at different temperatures.
Figure 3. Binary Fe-Cr phase diagram.
**Figure 4.** Content of N obtained by analysis of different zones on surface of metal specimens (Exp. 1b) containing the new phase (Type 1).
Figure 5. Content of N obtained by analysis of different zones on surface of metal specimens (Exp. 2b) containing the new phase (Type 2).
Figure 6. Content of N obtained by analysis of different zones on surface of metal specimens (Exp. 2c) containing the new phase (Type 3).
Figure 7. Content of N obtained by analysis of different zones of metal matrix and different new phase crystals on surface of metal specimens.
Figure 8. Schematic illustration of the relationship between the morphology of a new phase precipitated in an Fe-20mass% Cr alloy, the content of N in local zones of the metal matrix and the cooling rate of metal specimens after heat treatment.
Figure 9. Thermo-Calc calculations based on total N-content of specimen. 50, 300 and 500 ppm of N. (L=liquid, G=gas)
Figure 10. Thermo-Calc calculations based on analysed N-content in precipitations, 0.6 and 1.0 wt% of N. (L=liquid, G=gas)